SYNTHESIS AND CHARACTERIZATION OF MOLYBDENUM BASED NANOPARTICLES FOR PHOTOCATALYTIC APPLICATIONS

A SYNOPSIS

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1. Introduction

The environment is now seriously threatened by the growing discharge of organic contaminants into the water system. Industrial dyestuffs and synthetic textile dyes contribute significantly to global chemical output [1]. The detrimental impact of wastewater contamination on both individuals and the environment is a significant environmental concern. These days, both humans and animals suffer from the overuse of antibiotics and their release into the environment [2]. Organic waste may be removed from urban wastewater using normal treatment facilities, but antibiotic contaminants cannot be oxidized. The most important medication for treating bacterial infections and other microorganisms is an antibiotic. Unfortunately, the increased demand for antimicrobial medications has a harmful impact on both people and the environment [3]. Many different types of antibiotics, including ciprofloxacin (CIP), diclofenac, sulfonamides, macrolides, and penicillin's, are frequently employed [4]. The second-generation fluoroquinolone antibiotic Ciprofloxacin (CIP) is one of them and is mostly used to treat bacterial infections and pulmonary illnesses in both humans and animals [5-7]. Only a portion of antibiotic medications are broken down by body metabolism once they are ingested by humans or animals; the remainder is released into the environment as pharmaceutical waste [8-9]. Antibiotic medication contamination of the aquatic ecosystem, even at extremely low concentrations, poses serious risks to both humans and soil-dwelling microbes. Therefore, it is urgently important to look for an efficient treatment to remove pharmaceutical drugs from the aquatic system that may have an impact [10]. However, if in the previous ten years colors were only obtained from natural sources, today more dyes are employed in a variety of dying and culinary sectors. The majority of synthetic dyes were thought to be carcinogenic [11]. Methylene blue, an azo dye, is sandwiched between them and has primarily been used in the food and cosmetics industries. While being applied, this dye produces the normal red to purple tint, which is more poisonous, cancer-causing, and mutagenic. Additionally, methylene blue has biological functions in addition to its traditional usage as a stain for several dye businesses. Methylene blue has recently been used in pharmaceuticals, calico printing, and as a pH indicator.

Chronic toxicity to bacteria, microorganisms, and aquatic vertebrates is caused by the long-term release of pharmaceuticals and dyes into the atmosphere by inappropriate disposal treatment from manufacturing industries or hospitals [12].

Conversely, a number of techniques have been used to remove dye pollution, including osmosis, thermal decomposition, ultrafiltration, electro-dialysis, disintegration, etc. Due to the contaminants' chemical durability, these conventional approaches have already been shown to be notably ineffective for managing waste water from synthetic dyes [13]. Photocatalysis, an ecofriendly system, is regarded as the effective method for the removal of dangerous pollutants. The nanomaterial's photocatalyst was also thermal gradient and environmentally friendly. However, because of their minimal cost, great chemical durability, and lack of toxicity, metal oxide semiconductors were one of the most potential materials [14].

Recent research has developed a significant fascination in metal molybdate compounds, or $MMoO_4$ (M = Co, Zn, Mn, Fe, Ni, etc.), due to their recent success as outstanding materials in a variety of domains [15]. The synergistic interactions between the various metal molybdate constituents have been utilized to successfully produce composite material with numerous metal molybdate compounds [16]. Today, a variety of useful manufacturing techniques have been employed to produce certain metal molybdate compounds, including hydro/solvothermal [17], coprecipitation [18, 19], sonochemical [20], combustion [21], sol-gel [22] and solid-state [23] techniques. In recent years, numerous studies on the synthesis of metal molybdate compounds have focused on sonochemical and hydro/solvothermal techniques.

One of the trendiest issues in the energy-storage domains is metal molybdates, which have a stable crystalline structure, redox behaviour, exceptional physicochemical parameters, and high charge transport [24–25]. Along with these benefits, metal molybdates can also provide direct current paths, reduce the charge-discharge time, increase the electrolyte-electrode interfacial interaction, restrict mechanically deterioration, accommodate volume growth, and contribute to ecological friendly, among other things.

As a result, each Mo^{6+} is encircled by four $^{\bullet}O_2$ and each Pb^{2+} is encircled by 8 $^{\bullet}O_2$ in $PbMoO_4$, which possesses a good crystallinity of the scheelite type [26]. With an energy gap of about 3.20 eV, this compound exhibits a distinct crystal structure and distinct energy band structure. Lead molybdate exhibits good visible light catalytic activity in addition to being extensively explored recently in the disciplines of optical equipment fabrication, photocatalytic activity, and chemiluminescence, among others. In this work, g-C_3N_4 has been widely used in a variety of photocatalytic applications due to its many beneficial qualities, including stability, environmental friendliness, oxidation strength, and low cost. On the other hand, the wide band of g-C_3N_4 limits its catalytic activity. Due to the rapid recombination of electron-hole pairs, the catalytic activity of g-C_3N_4 with a broad bandgap is likewise minimal. This wide bandgap semiconductor can be combined with a suitable narrow bandgap semiconductor to overcome these problems, creating a highly effective photocatalyst that might act as a visible-light-driven catalyst.

Bismuth molybdate (Bi_2MoO_6) has attracted considerable interest of researchers due to its excellent response to the visible light and controllable morphology based on alternating layer structure of MoO_4^{2-} and $[Bi_2O_2]^{2+}$ [27, 28]. Many research works have been conducted to construct high-efficient Bi_2MoO_6/TiO_2 composite system, but its photocatalytic activity under weak visible light was still rarely concerned [29-31]. Under the weak-visible-light irradiation, there are fewer photo-generated carriers formed during the photocatalytic process than that under the strong-light irradiation, so the efficient capture and utilization of the visible light are more important in the weak-light irradiation photocatalysis. Unfortunately, the rapid recombination rate and poor transport properties of photogenerated charges restrict significantly the use of Bi_2MoO_6 for large-scale applications. Various strategies have been implemented to tackle these issues, among which the fabrication of Bi_2MoO_6-based heterojunctions with a suitable band structure has shown great potential. In particular, the Z-scheme heterojunction photocatalytic system, where charge transfer between two or more semiconducting photocatalysts relies only on the internal electric field (E) and not on a transfer mediator, has gained a great deal of interests [32]. In this regard, direct Z-scheme Bi_2MoO_6-based photocatalysts such as Bi_2MoO_6/V_2O_5 have been exhibiting promising performance.

Molybdenum trioxide (MoO_3) is one of the several metal oxide semiconductors which is already considered as the promising candidate for replacing TiO_2. The molybdenum trioxide, as an n-type semiconductor, is one of the most intriguing transition metal oxides [33, 34]. Over the past decades, MoO_3 has been widely investigated due to its properties like electrochromism [35, 36], gasochromism [37], photochromism [36, 38, and 39], photocatalytic performance [40] and capacitive behavior [41]. There are several well-developed processes and synthesis methods of MoO_3 that lead to various morphologies of this metal oxide. Zinc oxide (ZnO) is a n-type semiconductor widely in various application such as batteries, solar cells, photo-electrochemical cells and photocatalyst. Moreover, it is an excellent supporting material for the photocatalyst. In fact, the efficiency of metal molybdate is enhanced by the addition of ZnO as a co-catalyst. MoO_3/ZnO, which behaves as useful material has promised in gaining extraordinary attention of researchers because of having huge surface area for the activity and flexibility for designing the nanocomposite in desired shape with no change in chemical properties and has unresolved biocompatibility [42].

2. Review of Literature

The decolorization of prescription pharmaceuticals and dyestuffs discovered in aquatic systems has been extensively researched. Researchers from all over the world are very interested in the removal of medicines and colors from effluent. The following is an overview of how several photo-degradation research activities have progressed:

Lei Zhang et al. developed a facile surfactant-free hydrothermal synthetic approach for the preparation of $PbMoO_4$ polyhedrons. According to experimental findings, the creation of $PbMoO_4$ polyhedrons with smooth surfaces is favoured by an optimal amount of glycerol, a high reaction rate, and a lengthy reaction period. It suggests that $PbMoO_4$ polyhedrons have improved UV-light-driven photocatalytic activities, which can be attributed to their improved light absorption and electron-hole pair separation efficiency. This study offers a simple, high-yield, and inexpensive route to the synthesis of $PbMoO_4$ polyhedrons in comparison to previous solution-phase synthetic methods [43]. $PbMoO_4$ materials with a significant

crystallinity level and a low average size of particles were effectively synthesised by D.B. Hernández-Uresti et al. using the microwave-assisted solvothermal and solvothermal methods. The indigo carmine, orange G, tetracycline, ciprofloxacin, and salicylic acid were effectively tested on the catalyst after being exposed to UV-visible light. These findings suggest that the particle size, which is the primary factor influencing the photocatalytic performance in contaminants destruction in aqueous, is the reason why PbH material has lower photocatalytic activity than PbMH material. On the other hand, a high crystalline structure was a contributing factor in the PbH sample's increased producing hydrogen. It is proof that $PbMoO_4$ is a viable option for producing hydrogen and degrading pollutants as a photocatalyst [44].

According to Piyada Suebsom et al., the photoreduction deposition process was successful in producing Bi_2MoO_6 nanoplates with Pd nanoparticles on top. Bi_2MoO_6 nanoplates were covered with metallic Pd nanoparticles. Bi_2MoO_6 crystal's phase, shape, and crystallinity are unaffected by the addition of Pd nanoparticles. By taking in photo-excited electrons, the loaded Pd nanoparticles contributed to increased photocatalytic activity. As a result, in Bi_2MoO_6, the separation of photo-induced electron-hole pairs was improved and the recombination of photo-induced electron-hole pairs was decreased. According to this study, heterostructure 10 percent Pd/Bi_2MoO_6 nanocomposites exhibit the best photocatalytic activity for breaking down RhB by 98.30% in under 90 minutes when exposed to visible light [45].

Using the electro-spinning technique, Petronela Pascariu et al. successfully create nanostructures of pure ZnO, MoO_3, and MoO_3-incorporated ZnO. The orthorhombic crystalline structure obtained for MoO3, the hexagonal wurtzite-type structure for pure ZnO, and a combination of these structures for the ZnO: MoO_3 composite nanostructure were all confirmed by the XRD diractograms. The optical characteristics of the generated MoO_3-incorporated ZnO samples were investigated using UV-vis spectrometer and steady-state/time-resolved fluorescence spectroscopy. For usage in the photocatalytic process of the aquatic rhodamine B dye concentration, the catalytic efficiency of the produced pure/MoO_3-incorporated ZnO nanostructures was examined under [46].

For effective photocatalytic activity and their biomedical applications, synthesis, manufacturing, and characterisation of MoO_3/ZnO heterostructure under mild hydrothermal conditions. The extremely effective, modified MoO_3/ZnO with good recycling properties is examined. This material also demonstrates that it is suited for the degradation of EB dye with the removal of heavy metals. The suggested process for heterostructure degradation also revealed that the degradation's ultimate byproducts are exceptionally biocompatible and ecologically benign with low toxicity. The research boldly ends by stating that the desired customised and synthesised MoO_3/ZnO is a multifunctional nanocomposite with plenty of opportunities for future research in the field of nanotechnology [47].

3. Objective of Thesis

Inspired by the abovementioned achievements, molybdenum oxide combined photocatalysts have been the subject of enormous curiosity in recent decades. Therefore, the development of molybdenum metal oxide and doped with different semiconductor materials for complete detoxification of pharmaceuticals and dyes into the water and soil environment is an interesting and necessary task. The aim and objectives of our work which include:

- To synthesize $PbMoO_4$@g-C_3N_4, Bi_2MoO_6@V_2O_5, MoO_3@ZnO using simple hydrothermal technique and characterized by various spectroscopic and analytical tools such as XRD, FTIR, FESEM, EDX, Elemental mapping, UV- DRS and XPS analyzes.
- To identify the photocatalytic activity of MoO_3@ZnO the degradation studies was carried towards the ciprofloxacin drug and methylene blue dye.
- To predict the photocatalytic activity of Bi_2MoO_6@V_2O_5 was calculated by the degradation of ciprofloxacin drug and methylene blue dye.
- To explore the photocatalytic activity of $PbMoO_4$@g-C_3N_4 towards degradation of hazardous ciprofloxacin drug and methylene blue dye under Visible light irradiation.

- To optimize the photocatalytic reaction parameters which affect the photocatalytic process such as catalyst concentration and initial pollutant concentration, effect of loading to get a better efficiency towards the degradation of organic pollutants.
- To study the photodegradation mechanism of drugs and dyes.
- To investigate stability, repeatability and reproducibility of as prepared photocatalyst.
- To investigate the reactive oxidative species for the degradation progress through radical scavenging experiment.

4. Research Problem

Humans and aquatic vertebrates both rely on water as a source of nutrition. A diverse variety of pollutants enter the water system as a result of the unrestrained population. Aside from that, massive amounts of pesticides are employed in farming activities to fulfill the following food demands. Toxins from the textile and pharmaceutical and food industries are hazardous to living things. Conventional processes like as precipitation, filtration, adsorption, initiated slime, and others were often used remove organic contaminants from waste water.

The experimental setup and resources required for precipitating and coagulate procedures are highly costly. Based on the chemical persistence of the contaminants, these conventional procedures already have demonstrated to be incredibly ineffective in the handling of polluted effluent. These approaches have caused some difficulty in removing all organic contaminants from sewage effluents. Photocatalysis process can solve that problem. Photocatalysis is a field that encompasses energy technology, nanomaterials, earth sciences, optics, material science, scientific analysis, and other related fields. Photocatalysis is a chemical process that uses light to stimulate a substance to modify the reaction rates instead of being difficult. Semiconductor materials have received much interest as photocatalysts due to their low gap between both the conduction and valence band. This is the most environmentally friendly method of furnishing that will assist everyone on the world.

5. Organization of Thesis

The thesis is composed of Seven Chapters, organized as follows:

The Chapter 1 contains a general introduction to photocatalysis and their classification is discussed. The introduction of water pollution and their effects are explained. Chapter 2 explains the literature survey of previous studies on the photocatalyst synthesis and photocatalytic decomposition of organic pollutants has been reported. The motivations and objectives of the current work are discussed. Chapter 3 deals with the required materials for the synthesis of nanocomposites and also discussed with the characterization techniques and the materials and methods for the preparation of nanocomposite. Chapter 4 to 6 describes the results and discussion about the as-prepared nanocomposites. Chapter 7 discusses the summary of the work done in this thesis.

Chapter 1: Introduction

In medicinal waste and industrial waste, however, ciprofloxacin pharmaceuticals and methylene blue pigment were thought to have strong antibacterial and anti-inflammatory capabilities. The ecological system has been put at serious ecological risk as a consequence.

Wastewater treatment is currently the subject of extensive study around the globe; however, there are difficulties because the device must be functional and economical. For the eradication of organic pollutants in secondary pollution-free waste water, catalysts have long been considered one of the best solutions for water treatment. It is a sustainable, affordable technology that is simple to use, replicates well, and is ecologically friendly. In this research work is view on synthesis of different metal molybdate nanocomposites with the coupling of various semiconductor materials like V_2O_5, g-C_3N_4 and ZnO, (1) MoO_3/ZnO nanocomposites, (2) Bi_2MoO_6 @ V_2O_5 nanocomposite, and (3) $PbMoO_4$ @ g-C_3N_4 nanomaterial.

Chapter 2: Review of Literature

Chapter 2 discussed the literature survey about the binary metal oxide based semiconductor nanocomposite for the photodegradation of organic pollutants were reviewed. The literature survey describes how the toxic pharmaceutical drug and dye pollutants were converted to non-toxic mineral acids, water and CO_2 molecules by utilized semiconductor nanocomposite as a catalyst.

Chapter 3: Materials and Methods

Materials:

This part describes the experimental details. Details of the materials and chemical reagents used in the present study are described.

Materials characterization:

This part detailed a brief explanation on the principles of the characterization technique and the photo reactors used will be done.

Chapter 4: Development of visible light driven nanorod-like MoO_3@ZnO nanocomposite: An affordable catalyst for the degradation of organic pollutants

An effective visible light catalyst was successfully fabricated from a nanorod-like MoO_3/ZnO (MZ) nanocomposite using a simple hydrothermal method for the decomposition of the Ciprofloxacin (CIP) and Methylene blue (MB). In addition to XRD, FT-IR, SEM, EDX-Color mapping, DRS-UV, and XPS analysis, a variety of other physicochemical measurements were used to validate the as-prepared MZ nanocomposite. These results confirm the synthesis of nanorod-like MZ composite by successive steps. A MZ nanocomposite was demonstrated to be a superior catalyst for the degradation of CIP and MB dye when exposed to visible light. It is evident that the MZ nanocomposite is more effective than the host material for the degradation of CIP and MB. Moreover, the stability and reusability of the MZ nanocomposite also exhibit better results. The degradation efficiency of the MZ nanocomposite is 97.68% and 97.47% towards the degradation of the MB dye and CIP drug.

Chapter 5: Construction of novel $Bi_2MoO_6@V_2O_5$ nanocomposite as Visible Light-Driven catalyst for degradation of organic pollutants

In this work, the novel $Bi_2MoO_6@V_2O_5$ nanocomposites (NCs) are made by hydrothermal technique. As-prepared $Bi_2MoO_6@V_2O_5$ NCs are systematically confirmed by different spectroscopic techniques, respectively. The SEM results reveal the surface morphology; the nanorod like V_2O_5 was evenly decorated on the pebble stone like Bi_2MoO_6 surface. The elemental compositions of the presenting elements Bi, Mo, V and O are confirmed by X-ray Photon Spectroscopic analysis. The catalytic performance of $Bi_2MoO_6@V_2O_5$ for ciprofloxacin (CIP) and Methylene blue (MB) degradation was very high compared to host materials under visible light embellishment. Moreover, the radical trapping experiment substantiates that hydroxyl ($^{\bullet}OH$) and superoxide ($O_2^{\bullet-}$) radicals play a vital role in CIP and MB abatements. This work will provide new in-depth insights into other photosynthetic nanomaterials with potential applications in the field of environmental compensation.

Chapter 6: Fabrication of Pebble stone-like $PbMoO_4@g\text{-}C_3N_4$ Nanostructure: Focus on Photo catalytic degradation of organic pollutants

In this work, the $PbMoO_4@g\text{-}C_3N_4$ nanocatalyst is synthesized by the hydrothermal way. The as-prepared $PbMoO_4@g\text{-}C_3N_4$ nanomaterial was confirmed by powder X-ray diffraction (P-XRD), UV–visible diffuse reflectance spectroscopy (UV-DRS), photoluminescence (PL), scanning electron microscopy (SEM) and Transmission electron microscopy techniques (TEM). The scanning Electron Microscope result indicates the layer with pebble stone morphology structure of $PbMoO_4@g\text{-}C_3N_4$ nanomaterials. The catalytic performance for as-synthesized nanomaterial was analyzed by the ciprofloxacin (CIP) and methylene blue (MB) dye degradation process. More interestingly, the as-prepared $PbMoO_4@g\text{-}C_3N_4$ material is having higher catalytic performance compared to the other previous $PbMoO_4$ nanoparticles reports with an efficiency of above 92%. The degradation mechanism and the reaction kinetics of nanomaterial were also investigated. The aforesaid results are strong enough to suggest the nanomaterial may be an effective catalyst for environmental application.

Chapter 7: Summary and Conclusions

This chapter summarizes the results reported in chapter 4-6 and recommends the possible ways to improve the present studies for future research in this field.

- MoO_3@ZnO
- Bi_2MoO_6@V_2O_5
- $PbMoO_4$@g-C_3N_4

The degradation of antibiotics drug Ciprofloxacin (CIP) and Methylene blue dye has been achieved in the presence of aforesaid catalysts under visible light irradiation. Based on the results, concluded that the MoO_3@ZnO nanocomposites showed excellent photocatalytic activity towards the degradation of methylene blue dye effluent under visible light irradiation (Table 1).

Table 1. Comparison of the as prepared nanocomposite for the degradation of organic pollutants under the illumination of UV and visible light

Catalyst	Morphology	Pollutants	Weight of Catalyst (g/L)	Irradiation Time (min.)	% of efficiency
MoO_3@ ZnO	Nanorod like poly-crystalline Structure	CIP MB	0.03	60 80	97.68 97.47
Bi_2MoO_6 @V_2O_5	Pebble stone-like nanorod structure	CIP MB	0.03	80 50	72.3 95.86
$PbMoO_4$ @g-C_3N_4	Pebble stone-like structure	CIP MB	0.04 0.03	100 50	92.82 72.1

*CIP- Ciprofloxacin; MB- Methylene blue

We hope that this research work could open a new pathway to guide the design of proficient and stable binary catalyst for the real-time remediation of lethal pollutants. Moreover, the catalyst exhibiting in real samples with high stability and feasible recovery, thus the proposed material is also good for commercial purposes.

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7. List of Publications

1. **M. Rajkumar**, M. Arunpandian, K. Leeladevi, P. RameshKumar, S. Arunachalam, Fabrication of Pebble stone like $PbMoO_4$ Nanostructure: Focus on Photocatalysis, photoluminescence and electron density distribution analysis, *Physica B: Physics of Condensed Matter*, **620** (2021) 413222.
2. **M. Rajkumar**, M. Arunpandian, K. Leeladevi, T. Veemaraj, S. Arunachalam, Synthesis of Novel $Bi_2MoO_6@V_2O_5$ Nanocomposite as Visible-Light-Driven catalyst for Degradation of Noxicious Methylene Blue Dye, *Journal of Materials Science: Materials in Electronics*, **33** (2022) 5816–5830, DOI: 10.1007/s10854-022-07765-1.
3. **M. RajKumar**, M. Arunpandian, K. Leeladevi, T. Veemaraj, S. Arunachalam, Development of visible light driven nanorod-like MoO_3@ZnO nanocomposite: An affordable catalyst for the degradation of organic dye moiety, *Applied Physics A*, **128** (2022) 558.